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In this proposal it is argued that the thermal stability of most jet fuels would be dramatically improved by the efficient removal of a fuel's dissolved oxygen (in flight). It is envisioned that a thermally activated reaction between the oxygen scavenging additive and dissolved oxygen will occur, in a controlled and directed manner, such that formation of insoluble thermal degradation products will be limited. To date our data has identified several potential additive candidates which meet our preliminary specifications. With continued funding suitable stabilizing additives for super-critical jet fuels will be developed.

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DEVELOPMENT OF STABILIZING ADDITIVES FOR SUPER-CRITICAL JET FUEL

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Abstract

Our current research program is in response to the U. S. Air Force's FY93 New Initiative entitled "Advanced Fuel Composition and Use." The critical goal of this initiative is to develop aircraft fuels which can operate under supercritical conditions. This is a vital objective since future aircraft designs will transfer much higher heat loads into the fuel as compared with current heat loads. In this proposal it is argued that the thermal stability of most jet fuels would be dramatically improved by the efficient in flight removal of a fuel's dissolved oxygen. The bulk fuel could be stabilized by the addition of an additive which will be judiciously designed and programmed to react with dissolved oxygen and produce an innocuous product. In addition, if the oxidized additive is also a good hydrogen atom donor it is envisioned that pyrolytic deposits will be limited. Consequently, fuel stability in both the sub-critical and super-critical regimes will be addressed. It is believed that successful completion of this project will result in the development of a new type of jet fuel additive which will enable current conventional jet fuels to obtain sufficient thermal stability to function in significantly higher temperature regimes.

1. Introduction

Currently, aircraft fuels have a practical temperature limit (325°F, 150°C) which cannot be exceeded without causing serious problems in the fuel system. If this temperature threshold is exceeded, the fuel chemically decomposes to form gums and solids which adversely affect the fuel system. Conventional wisdom posits that these fuel deposits are the end result of a sequence of complex chemical reactions that are thermally promoted between oxygen dissolved in the fuel and certain "reactive" fuel molecules.[1] If this paradigm(i.e. conventional wisdom) is correct then efficient removal of oxygen from the fuel would limit the oxidative

break down of the fuel. Consistent with this view is the general observation that purging a jet fuel of dissolved oxygen usually will result in a tremendous improvement in the thermal stability of that fuel.[2]

Recent studies have revealed that most of a fuel's dissolved oxygen is consumed by chemical reactions which initially produce peroxides at temperatures between 150-260°C.[3] In addition, Classical chain-breaking donor antioxidants (i.e. substituted phenols and phenylene diamines) usually do not inhibit deposit formation when a fuel is stressed at temperatures of 150-250°C.[4,5]

Consequently, the sub-critical oxidative stability of jet fuels is currently problematic. It is imperative that this problem be rectified in order that future aircraft fuels possess adequate thermal stability to enable them to achieve supercritical conditions with minimal degradation within the fuel system. It is proposed herein that the efficient removal of dissolved oxygen from jet fuels during flight might provide the necessary improvement in sub-critical fuel stability. If this line of reasoning is correct, then the fundamental problem can be reduced to the problem of removal of a fuel's dissolved oxygen before it contributes to the thermal degradation of the fuel.

There are two fundamentally different approaches to the removal of dissolved oxygen from a jet fuel during flight. One approach would be to utilize a technological solution (on board purging), while another approach would be to effect a chemical solution. We envision the chemical solution to entail adding a specifically designed fuel additive (concentration 200-400 ppm) to the jet fuel. Theoretically, this additive would chemically react (as the temperature of the fuel increases) with the dissolved oxygen and thus remove it, in an innocuous manner, from the fuel during flight. In this manner the jet engine would receive its fuel with minimal dissolved oxygen (hence the fuel will have high thermal stability), and there would not be any "unnecessary" (i.e. purging technology) payload added to the aircraft.

The focus of our research program is to explore the fundamental chemistry necessary to develop potential fuel additives (candidates) that will function as thermally activated oxygen scavengers. It is envisioned that successful completion of this project will result in the development of a new type of jet fuel additive which will enable current conventional jet fuels to obtain sufficient

thermal stability to function as " JP-900" fuels. In addition, it is postulated that the successful development of thermally activated oxygen scavengers will also provide the sub-critical thermal stability necessary for future endothermic fuels. This is a **vitally important objective** since it is now clear that most of a jet fuels thermal oxidative degradation occurs at sub-critical temperatures. In addition, it conceivable that a properly designed additive will also enhance fuel stability in the super-critical regime. Coleman[6] has shown that at temperatures > 400C, where fuels tend to pyrolytically degrade, hydrogen donors like benzyl alcohol can significantly limit deposits. Consequently, it would be prudent to design such functionality into the final additive.

II. Experimental Section

All experimental details have been previously described. [7]

III. Development of Stabilizing Additives for Super-Critical Fuels

Contained in this section is a logical articulation of our approach to the development of stabilizing additives for super-critical fuels. For clarity this section is divided into 2 parts; with part A developing and establishing the necessary presuppositions and the overall thinking. Presented in part B is our preliminary results to date.

IIIA. Conceptualization of Idea

In Scheme 1 is presented a generalized design concept for a super-critical fuel stabilizing additive. The ideal additive would provide both sub-critical thermal oxidative stability and super-critical pyrolytic stability. As indicated in Scheme 1 there are at least 3 properties of a successful additive. The additive must react selectively with the dissolved oxygen, must remain dissolved in the fuel and should be a good hydrogen atom donor. Probably, the most difficult property to obtain is the oxygen selectivity of the additive. This is the only property that this proposal will address. The latter two aspects of the problem will be addressed in a future proposal.

In Scheme 1, step A, the additive (SH) is thermally promoted to **selectively react** with the fuels dissolved oxygen. In step B the oxidized additive (the primary

oxidation product) is spontaneously convert into a molecular structure that is thermally more stable (the secondary oxidation product). Idealy, the secondary oxidation product (OSOH) would serve as a good hydrogen atom donor since these types of compounds are known to minimize pyrolytic decomposition. In this manner the additive addresses fuel degradation both in the sub-critical and super-critical regimes.

The idea conceptualized in Scheme 1 is predicated upon the following observations concerning jet fuel degradation, as indicated by both peroxide and insolubles formation:

(i) Taylor [8] has reported in his 1974 study, at least for the two jet fuels examined, that reduction of the dissolved oxygen content from air-saturated values (~60ppm) to less than 15ppm, decreased deposit formation produced under supercritical conditions by greater than 50% (when compared to similar deposit levels produced without oxygen removal).

(ii) insoluble formation increases with temperature and at < 300°C, tends to involve reactions of trace indigenous heteroatom containing molecules (S,N, and O)(i.e. natural antioxidants) with dissolved oxygen. [9]

(iii) most of the oxygen consumption by the bulk fuel and concomitant peroxide formation occurs at temperatures between 150-260°C, after the natural antioxidants have been consumed. [9]

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(iv) at temperatures >400°C, most fuel insolubles tend to be produced by pyrolysis reactions. [10]

If the above stated observations and interpretations are correct, and if it is possible to extrapolate aspects of low temperature autoxidation (i.e. 50-100°C) into the temperature regime of 100-150°C, then in Scheme 1 is wedded a logical approach to significantly enhance both sub-critical and super-critical jet fuel stability. Inherent in the design of Scheme 1 is the presupposition that most of the fuels dissolved oxygen will preferentially react with the fuel additive.

Consequently, the fuels dissolved oxygen can be selectively placed into a molecule that is designed to accommodate it safely. There are two different approaches towards designing additives that will selectively react with oxygen.

The first approach to the selectivity problem would be to capitalize on the natural peroxyl radical chain mechanism for the fuel thermal oxidative degradation. For this approach to work it is neccessary that the additive (S-H) bond be weaker than similar bonds in the fuels natural antioxidants (see (ii) above). Thus, owing to the selectivity of the peroxyl radical, the fuels dissolved oxygen would primarily be incorporated into the additive rather than the natural antioxidants.

The second approach to the selectivity problem requires a direct reaction of the fuels dissolved oxygen with the additive before the start of the fuels natural peroxyl radical chain mechanism for thermal oxidative degradation. This mode of reaction is equivalent to the ETIO concept which has been previously discussed in the literature. [11]

In both of the above approaches the net effect of a properly functioning additive is the removal of the fuels dissolved oxygen without inducing reaction with the fuels natural antioxidants. Therefore, we define the following experimental criteria for a sucessful additive candidate at this stage of the project:

> (i) the rate of autoxidation of a potential additive candidate must not be inhibited by the presence of antioxidants.

> (ii) the antioxidants must not be consumed during the course of the additive candidates autoxidation.

IIIB. Preliminary Data

In table 1 is compiled preliminary results for an initial rate study of the autoxidation of various potential additive candidates. The note worthy feature is that two of the five candidates, triphenylphosphine (TPP) and phenalene, are deamed as viable additive candidates. This is based upon these candidates

meeting criteria (i) and (ii) above. The data to date supporting this claim is presented in tables 2-4.

Fluorene was found not to be a viable additive candidate since its autoxidation can be totally inhibited by BHT under our experimental conditions (table 1).

The situation with dimethyl and trimethylpyrroles, DMP and TMP, respectively, is more complicated. As shown in table 5 the presence of BHT suppresses DMP oxidation around 40% while TMP is similarly inhibited by only 11%. Presumably, there are two concurrent pathways for pyrrole autoxidation. There seems to be a peroxyl radical-chain pathway which can be inhibited by BHT. In addition, there is a pathway that is not inhibited by BHT. Our data suggests, that changing the pyrrole structure from DMP to TMP makes the latter pyrrole a much better additive candidate. It is likely that if tetramethylpyrrole is examined next that another successful additive candidate will be identified. In table 6 is presented additional data on the selectivity of the TMP autoxidation. In this experiment one equivalent of fluorene was added to the system to test for the presence of hydrogen atom abstracting radicals. The C-H bond in fluorene has double benzylic activation and is very weak. If hydrogen abstracting radicals are generated during TMP autoxidation, it is anticipated that they would promote the facile oxidation of fluorene into fluorenone. Apparently, such radicals are not present in TMP autoxidation since fluorene was not oxidized.

Conclusion

In this proposal it is argued that the thermal stability of most jet fuels would be dramatically improved by the efficient removal of a fuel's dissolved oxygen (in flight). It is proposed herein to stabilize the bulk fuel by the addition of an additive which will be judiciously designed and programmed to react with oxygen and produce an innocuous product. Consequently, it is envisioned that a thermally activated reaction between the oxygen scavenging additive and dissolved oxygen will occur, in a controlled and directed manner, such that formation of insoluble thermal degradation products will be limited.

To date our data has identified several potential additive candidate which meets our preliminary specifications. With continued funding suitable stabilizing additives for super-critical jet fuels will be developed.

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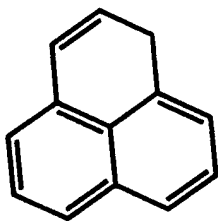11. B. Beaver, Fuel Sci.&Tech. Int'l., 1991, 9, 1287.

Sample Additive Candidates
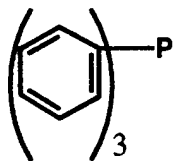
triphenylphosphine (TPP)
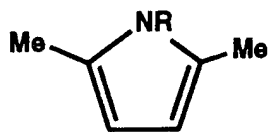
dimethylpyrrole DMP; R=H

trimethylpyrrole TMP; R=Me

Phenalene
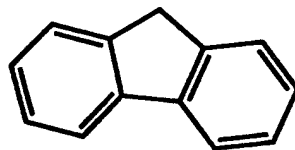
Fluorene

Scheme 1

Ideal Additive for a SC Fuel

$$S\text{-}H + O_2 \xrightarrow[\text{heat}]{\boxed{A}} S\text{-}OO\text{-}H$$

$$\Big\downarrow \boxed{B}$$
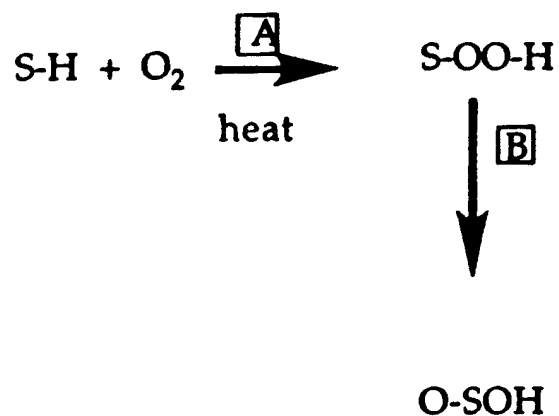
$$O\text{-}SOH$$

PROPERTIES

1. S-H must be selectively oxidized in the presence of BHT

2. Proper solubility for O-SOH

3. O-SOH must be a good hydrogen donor

Table 1

Reaction Order Data for Additive Candidates

Substrate	Additive(s)	Solvent	Temp. $^\circ$ C	Subs. order	O_2 order
fluorene	none	dodecane	165	not det.	0.8
fluorene	BHT	dodecane	165	no Rx.	no Rx.
DMP	none	dodecane	120	0.9	0.6
DMP	BHT	dodecane	120	0.5	0.9
TMP	none	dodecane	120	1.1	0.6
TMP	BHT	dodecane	120	1.0	0.5
TPP	BHT	dodecane	150	1.1	1.2
TPP	BHT	decalin	150	1.0	1.3
Phenalene	BHT	cyclooctane	100	1.0	0.9

Table 2
Initial Rate of Oxidation for tri-Phenylphosphine at 150°C

Solvent	Additive (eqs.)	Int. rate of loss
dodecane	none	1.24×10^{-4}
dodecane	1 x BHT	1.36×10^{-5}
dodecane	2 x BHT	1.70×10^{-5}
dodecane	3 x BHT	1.57×10^{-5}
trichlorobenz.	1 x BHT	3.24×10^{-5}
decalin	1 x BHT	1.03×10^{-5}

Table 3

Initial Rate of Phenalene Autoxidation in O_2 Saturated Cyclooctane at 100^0C in the Presence of 2Eq. BHT

Solution	Rate of phenalene oxidation(M/min)
Phenalene(0.01464M)	3.5×10^{-6}
Phenalene(0.01464M)/BHT (0.02048M)	3.3×10^{-6}

BHT doesn't inhibit the oxidation of phenalene

Table 4

BHT Concentration as a Function of Time in the Autoxidation of Phenalene in Cyclooctane at 100^0C

Time(min)	Con. of BHT(M)
0	0.05236
120	0.05248
240	0.05240
360	0.05243

BHT is not consumed

Table 5

Effect of BHT on the Initial Rate Pyrrole Autoxidation at 120^0C with O_2 Sat. Solvent

Solution	Rate of pyrrole oxidation(M/min)
TMP(0.01984M)/Cyclooctane	4.6×10^{-5}
TMP(0.01984M)/Cyclooctane/ BHT(0.04421M)	4.1×10^{-5}
DMP(0.01978M)/Dodecane	6.2×10^{-5}
DMP(0.01978M)/Dodecane/BHT (0.04026M)	3.7×10^{-5}

BHT partially inhibits the oxidation of DMP

BHT slightly inhibits the oxidation of TMP

Table 6

Initial Rate of TMP Autoxidation in the presence of Fluorene and BHT in Dodecane at 100^0C.

Time(min)	Con. of Fluorene(M)	Con. of TMP (M)
0	0.03866	0.03628
30	0.03848	0.03500
60	0.03865	0.03384
90	0.03851	0.03274
120	0.03885	0.03209
150	0.03853	0.03144
180	0.03870	0.03062

TMP is selectively oxidized